Liquid structure changes of Bi under different melt states

Ziyang He[a,†,*], Chen Liang[b,†], Guoqiu He[b]

[a]Department of Industrial and Manufacturing System Engineering,

Iowa State University, Ames, IA 50011 USA.

[b]Department of Material Science, Tongji University, Shanghai 201804, China.

† Z.H. and C.L. are joint first authors.

*Corresponding Author:
Ziyang He
Email: heziyang@iastate.edu
Address:
Department of Industrial and Manufacturing System Engineering,
Iowa State University, Ames, Iowa 50014, USA.

Abstract This paper is focused on the relationship between solidification and melt sates. An abnormal change which takes place at 744 °C from 84 to 120 min indicated a liquid-liquid structure transition in pure Bi melt. Based on liquid-liquid structure transition, experiments of pure Bi were carried out. Cooling from different melt states, the solidification behaviors and structures changed a lot, such as undercooling, solidification time, grain sizes and the number of twins and pedestal sits. Especially, as a semi-metal, a liquid-liquid structure transition greatly increases the metallicity of Bi, and during the solidification Bi turned from smooth to coarse solid/liquid interface.

Key words: liquid-liquid structure transition, Bi melt, twins, pedestal sits, solid/liquid interface.

1 Introduction

As a Group-V element, Bi is semi-metal; it both has the properties of metal and non-metal elements. It has great usage in such as making fusible alloys as metal form, compound form used in medical. Besides, it also can be used in semiconductor and thermoelectric materials combined with some elements. Based on the wide usage, the investigation in liquid/solid state on Bi metal is becoming more and more appealing [1–8] .

According to the prior work, there is a liquid-liquid structure transition in Bi melt. Recently, liquid bismuth structure has been observed to change abruptly with temperature increasing. Using neutron diffraction measurement [9][10] and thermal analysis [10], Greenberg et al. observed that coordination number abruptly decreased at 740 °C and its endothermal nature was revealed at the same temperature. Wang et al. presented the discontinuous point of liquid bismuth viscosity, which occurs at 480 °C [11]. Greenberg et al. used sound velocity (SV) measurement [12] to reveal that SV value remains a constant from 271 °C to 330 °C, and that SV-T curve deviated from linearity at about 700 °C. These experimental results indicated that the liquid bismuth structure vary much with temperature increasing.

There are different solidification manners: facet (smooth interface), facet/ non-facet, non-facet (coarse interface) [13]. As a typical semi-metal, Bi grains will grow in two different manners under various solidification conditions. Although the influencing factors on solidification manners have been studied for many years, a lot of phenomena and results cannot be explained accurately. So there is a long way to explore the solidification manners and learn its rules.

As known, solidification behaviors and structures are determined by liquid structure [14–16]. Dose the liquid structure transition in Bi have great influence on the solidification structure? Based on this question we carried out a series of experiments to find out the relationship between the two factors.

2 Experiment

The samples were prepared from 99.99 % pure bismuth, which were melted at 450 °C for 30 min, then poured into measuring cells before cooling down to room temperature for the following experiments. The experimental details and equipment had been described in [17]. The whole measuring process was under the protection of pure argon (5N). Isothermal experiments were made on Bi melt held at 744 °C for 290 min. The curves of resistivity versus time ($\rho - t$) were recorded, as shown in Figure 1.

The samples were melted in Al_2O_3 crucibles and protected by B_2O_3 in the electrical resistance furnace. Each experiment used the equiponderant B_2O_3. The melting and holding temperature points and time were chosen according to the electrical resistivity experiment results, 744°C - 50 min and 744°C - 120 min. In order to track the thermal history of the alloys during cooling, the cooling curves were recorded as shown in Figure 2. Furthermore, by using Newton thermal analysis, the parameters of solidification behaviors calculated were list in Table 1. For convenience, the two specimens cooled from 744°C - 50 min and 744°C - 120 min were named samples A and B. The two samples were observed with the optical microscope (OM) and scanning electron microscope (SEM) in order to study the structure changes and rules.

3 Results and discussion

In Figure 1(a), the temperature always remains at 744±2 °C, but in Figure 1(b) the resistivity begins to descend at 84 min and ends at 120 min. As a sensitive parameter, resistivity change indicates the liquid-liquid structure transition in Bi melt, and in prior work liquid-liquid structure transition has been confirmed in Bi melt by many ways [18, 19]. So it is reasonable to deduce that there is liquid-liquid structure transition in the time from 84 to 120 min at 744 °C for Bi melt.

The cooling curves are shown in Figure 2 and the solidifications characters calculated by Newton method are list in Table 1. The undercooling of samples A and B are 7.1 and 16.6 °C, respectively. The solicitation time, maximum of solidification rate and solidification acceleration

enlarge when the melt experiences liquid-liquid structure transition.

The solidification structures are shown in Figure 3. From Figure 3, we can see that the twins in sample B are much more than those in sample A. Furthermore, in order to explore the growth mechanics, the high resolution SEM pictures are shown in Figure 4 and Figure 5. The lamella and pedestal sits can be clearly seen in the solidification microstructure.

Considering the resistivity change in isothermal experiment, and combing the prior work about Bi melt, we can deduce that there is liquid-liquid structure transition in Bi melt in the time interval of 84 to 120 min at 744 °C. It means in this process the remained atomic bonds of crystals after melt point break up into smaller, more disordered and relatively homogeneous new short range orders [20][21]. So the melt becomes more homogeneous and disorder.

Broadly, there are no heterogeneity but homogeneity nucleation cores in pure Bi solidification. In the melt, which does not underwent the liquid-liquid structure transition, the remained atomic bonds of crystals can serve as nucleation cores, so the melt can start nucleating at relative higher temperature; while in the other samples, the atomic bonds are smaller, as a result they can only start nucleating at a lower temperature, so it needs greater undercooling.

By SEM method, lamellar microstructures in the two different melt states of Bi are observed, shown in Figure 3. As a semimetal, Bi has smooth solid/liquid interface in solidification process, so it is hard for the atomic adherence to the surface and the rates of growth in different the crystal planes. At the present time, we use smooth solid/liquid interface growth mechanism to explain the growth of lamellar structures. Through observation of the two samples surface, there are no screw dislocations and two-dimension crystal nuclei indicating the vicinal surface growth mechanism is main growth of Bi. In sample B, it is easy to observe two micron pedestal sits as shown in Figure 4. These large-scale pedestal sits are formed from signal atomic pedestal sit gathering when moving in the smooth solid/liquid interface.

There must be pedestal sits as long as the vicinal surface exists due to anisotropy of interfacial energy. In Figure 4, the black dotted line expresses vicinal surface, and it can be seen that there are obvious pedestal sits. As a result, the growth of vicinal surface is the pedestal sits moving on the singular surface (smooth solid/liquid interface expressed by white dotted line). As far as we know the solidification manners will turn from facet to non-facet with driving force increasing. At the same time, as the anisotropy of edge energy for the narrow and long interface, the pedestal sits will kink denoted by the white arrow in Figure 4 [22]. During crystal growth, the particles in the kink position have the lowest potential energy and most stabilization. The lamellar structures sweep from kink position to singular surface.

At present, the view point of the cluster getting smaller and more uniform after temperature induced liquid-liquid structure transition has achieved agreement. The cluster structure research indicates that the fewer atoms in the clusters, the less type of clusters will be discovered. Based on this point, the difference between the cluster structures become smaller after liquid-liquid structure transition, that is the similarity ratio getting lager and structure fluctuation getting smaller. Considering about the correlation between liquid-solid structures, we can draw a conclusion that liquid-liquid structure transition inevitably affects the solicitation structures. In the solidification process, liquid atoms or clusters will change into solid crystal lattice. If the liquid cluster similar to solid crystal structure, atoms in liquid/solid interface match well, so it has low interface energy and liquid clusters are easy to deposit onto solid surface. The interface may exist as coherent twins plane after solidification. If twins form as this mechanism, twins in sample B must be more than in sample A. The experiment results confirm this mechanism, as shown in Figure 5. On the other hand, the most of twins are caused by pedestal sits, it means pedestal sits are also more in sample B than in sample A. When the density of pedestal sits gets large, there is a tendency of change from smooth to coarse interface. As a result in pure Bi turns from semi-metal to metal properties. This thought can be testified if there will be the large resistivity in the melt after liquid-liquid structure transition.

4 Conclusion

Through the investigation on resistivity of Bi as a function of holding time at 744 °C, we can draw a conclusion that there is liquid-liquid structure transition in Bi melt. Besides, solidification behaviors and structures changes a lot after different melt treatments such as undercooling, solidification time, grain sizes and the number of twin and pedestal sits. Importantly, Bi greatly increases the metallicity after liquid-liquid structure transition, and turns from smooth interface to coarse interface during solidification.

Acknowledgements

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Figures and tables

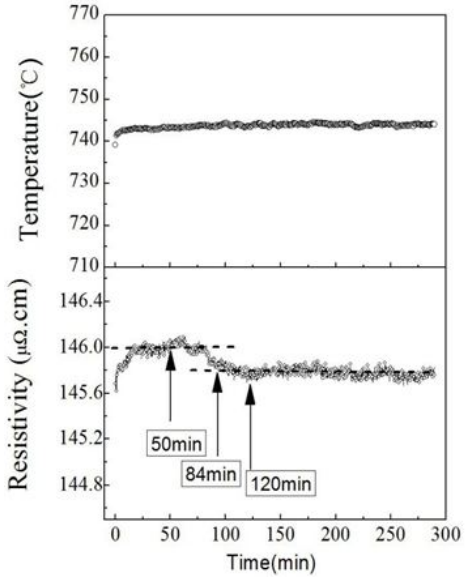

Fig. 1: The resistivity-time curve of pure Bi at 744°C

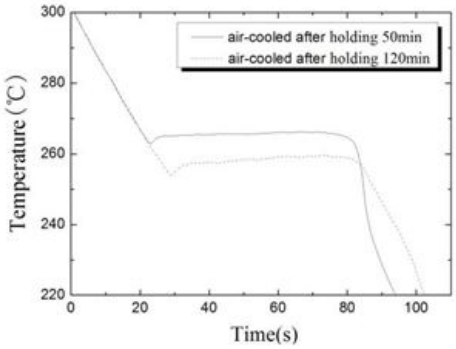

Fig. 2: Air cooling curves of pure Bi before and after liquid structure change

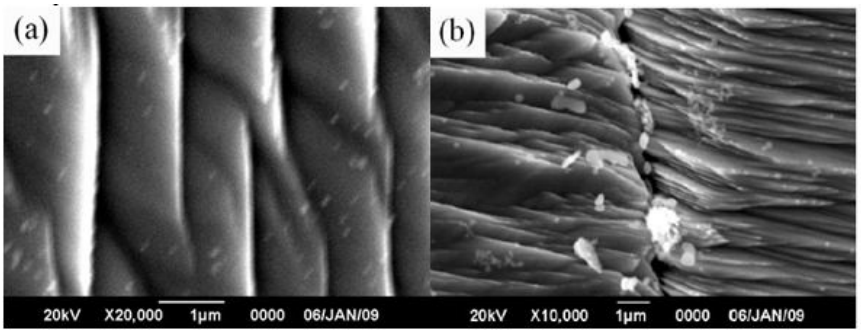

Fig. 3: Lamellar structure of pure Bi before (a) and after (b) liquid structural change

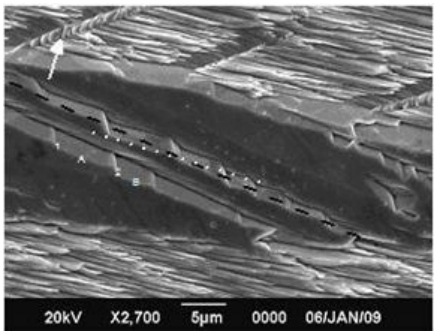

Fig. 4: Step bunching of pure Bi after liquid structural change

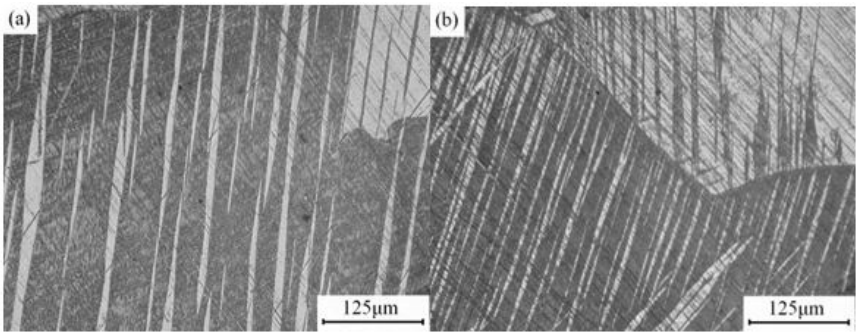

Fig. 5: Number of multiply twin of Bi before (a) and after (b) liquid structural change

Table 1: Eigenvalues of solidifications for pure Bi before and after liquid structure change

Holding time (min)	Variable	50	120
Start of solidification	T_{ss} (°C)	264.3	254.8
	t_{ss} (s)	21.6	28.08
End of Solidification	T_{es} (°C)	263.6	226.96
	t_{es} (s)	84.78	99.9
Undercooling of nucleation start (°C)	ΔT_L (=T_L-T_{ss})	7.1	16.6
Solidification time (s)	t_{ss} - t_{es}	63.18	71.82
Maximum of solidification rate (10^{-2}/s)		3.23	4.69
Solidification acceleration (10^{-2}/s^2)		1.4	2.05